



Electrochemical polymerization of aniline on carbon–aluminum electrodes for energy storage

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HIGHLIGHTS

- A new energy storage electrode, based on a composite of Al/C/PANI is reported.
- Synthesis occurs in aqueous media and is transferable to non-aqueous environments.
- Charge/discharge performance studies show similar performance as Pt/PANI electrodes.
- The specific capacity for the Al/C/PANI films are >125 mAh g⁻¹.

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ABSTRACT

We report a simple and reliable method to electrochemically synthesize PANi on aluminum carbon (Al/C). Aluminum electrodes were coated with hard black graphite. Polyaniline was then deposited in steps from +0.75 V to +0.825 V (V vs. Ag/AgCl) in low pH growth solutions containing aniline and camphor sulphonic acid. The polyaniline films were rinsed in hydrazine solution and dried in an infrared oven under a nitrogen atmosphere. The films were transferred and are stable in a 50:50 (v/v) propylene carbonate (PC)/acetonitrile (ACN) solvent mixture containing 0.5 M LiClO₄ electrolyte. Cyclic voltammetry and charge-discharge capacities are reported. Microscope (SEM) images of Al/C/PANI and Pt/PANI films show similar structural details and morphology. The specific capacity for Al/C/PANI in nonaqueous solutions was ca. 133 mAh g⁻¹, in good agreement with the reported data for other PANi-based electrodes. The performance studies and SEM images demonstrate similar results for Pt/PANI and Al/C/PANI electrodes.

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1. Introduction

Current commercial cathode materials include relatively expensive metal oxides such LiFePO₄, LiNiO₂, LiMn₂O₄ and LiCoO₂ [1]. The percentage of lithium, on a mass basis, which is available in these cathode materials is strikingly low: 4.4%, 7.1%, 3.9%, and 7.1% respectively. The resulting extra mass of unavailable lithium decreases the gravimetric capacity. In contrast, polyaniline (PANI) is an inexpensive, light-weight, Li-free cathode materials offering potentially several significant advantages in the fabrication of Li-ion rechargeable batteries. PANi films on metal as well as other substances, including carbon and indium tin oxide, have recently been of great research interest in the field of rechargeable energy storage devices [2–9]. PANi is popular because of its ease of synthesis, high thermal, electrical and chemical stability, and better

conductivity [10–12]. To be compatible with lithium based energy storage devices, PANi films on metallic current collectors must operate in non-aqueous environments. In general, non-aqueous growth of PANi on metals has been challenging. Aqueous electrochemical deposition of PANi on inert surfaces such as Pt, followed by transfer to non-aqueous solvents, has been demonstrated [13]. However, use of less expensive and light-weight materials for energy storage devices is desirable from an economic point of view. One approach is to use aluminum (Al), a low density, inexpensive and abundant metal, as the current collector. Electropolymerization of PANi on Al in aqueous solution is problematic because in the potential range where aniline polymerizes, any exposed metal surfaces give rise to the hydrogen evolution reaction, preventing uniform PANi growth. Hydrogen evolution at an Al electrode surface occurs between –2.0 V and +0.6 V vs. the saturated calomel reference electrode [14]. Not surprisingly, numerous methodologies have been proposed to overcome hydrogen evolution at Al surfaces in aqueous acidic media during electrochemical treatment

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and preparation of Al/PANI electrodes for charge storage electrodes as well as for protection against corrosion [14–22].

Motheo et al., reported a chelation method to electropolymerize PANI films on Al surfaces using alizarin as a chelating agent [19,21,23]. An important finding of this work is that the method of chelation with alizarin suppressed hydrogen evolution in aqueous solutions and increased the current efficiency for the PANI deposition during the electropolymerization. It was also noted that the method works best with oxalic acid in the growth solution along with aniline [19,23]. However, these electrodes do not withstand transfer to nonaqueous solvent. Since alizarin is soluble in organic solvents, we have found that the PANI films detach when immersed in an organic solvent [24].

Another method, as reported by Habibi et al., is to first coat Al with Pd by dipping a cleaned Al surface in a $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ solution for a given time [18]. A uniform Pd coating is then formed on the Al surface. The resulting Pd/Al electrodes can be used successfully to electrochemically grow PANI without hydrogen evolution. However, the cost of Pd makes Pd/Al electrodes prohibitively expensive to use in non-aqueous Li-ion batteries. Finally, the electrochemical response of graphene-polyaniline conducting polymers prepared by chemical precipitation has recently been reported [25].

In this paper, we describe a simple and reliable method to electrochemically synthesize PANI on aluminum carbon (Al/C) surfaces in acidic aqueous solutions. The resulting PANI films are stable upon transfer to non-aqueous solvents. Charge/discharge performance studies and SEM images are presented and compared to PANI/Pt electrodes.

2. Experimental

2.1. Chemicals and instrumentation

All the chemicals used in this study were purchased from Sigma–Aldrich and used as received except aniline, which was distilled under reduced pressure and stored at 4 °C. Acetonitrile (ACN) and propylene carbonate (PC) were purchased as anhydrous solvents. LiClO_4 was battery grade. Non-aqueous electrolyte preparation and electrode testing were carried out in an argon (Ar) filled custom built Terra-Universal Glove Box, Series 100, Model 1689-00D at –40 to –60 °F dew point, monitored by Dewpoint Transmitter DMT 242, Serial F5040002. Electrochemical experiments were conducted on Princeton Applied Research (PAR) 273 and 273A potentiostats, and a MACCOR 4000 multichannel instrument. All aqueous solutions were prepared by using deionized (18 MΩ) water (DIW) purchased from Fisher Scientific after degassing for 2 h. All voltages reported are vs. a Ag/AgCl reference electrode unless otherwise noted.

2.2. Preparation of the Al/C electrode

Aluminum 1100 or 5052 series alloys of 20 micron and 10 micron thicknesses, respectively, were cleaned with acetone, and rinsed with DIW thoroughly to clean the surface. Attachment of a graphite linker on the clean Al surfaces was carried out by using two different methods.

The first method was by rubbing the cleaned Al surface with an HB #2 pencil until the surface was covered by graphite. Other #2 pencils gave similar results. It is important to avoid deep surface scratches during this process. Prior to electrochemical polymerization, the Al/C surface was wiped with a KimWipe to remove excess graphite and trimmed to an area of $1 \times 1 \text{ cm}^2$, leaving an uncoated tail for attachment of an alligator clip. The edges of the

$1 \times 1 \text{ cm}^2$ Al/C materials were darkened with a pencil to ensure coverage on the edges.

The second method utilized an RYOBI Model #P400 orbital sander. Graphite (TIMREX, HSAG 300) was deposited on a cleaned Al surface by using the orbital sander for approximately 2 min per side at a rate of 11,000 orbits/min. A gray-black Al/C surface was obtained, trimmed to a $1 \times 1 \text{ cm}^2$ sample and the edges were coated with graphite from a pencil, as described above. PANI deposition was limited to the carbon-coated surface by immersing only the $1 \times 1 \text{ cm}^2$ area in the growth solution.

2.3. Electrochemical polymerization of PANI on Al/C electrodes

Al/C electrodes were inserted into a single compartment electrochemical cell and used as the working electrode. Two Pt counter electrodes were placed on either side of the working electrode (about 5 mm distance) and the Ag/AgCl reference electrode was placed close to the Al/C working electrode. Preparation of 100 ml of growth solution containing 0.45 M aniline, 0.1 M camphor sulfonic acid (CSA) was carried as follows: CSA was added to ca. 60 ml of DIW; next aniline was added and the mixture was stirred until a clear solution was formed; finally the pH was adjusted by dropwise addition of 6 M H_2SO_4 . When the pH was near the desirable level (~1.3), DIW was added to bring the total volume to 100 ml. Electrochemical polymerization was carried out by adding 20 ml of the growth solution to the electrochemical cell.

A potential-step method was used to electrochemically deposit PANI on Al/C electrodes. The initial potential was set to +0.750 V and the potential was increased as the columbic growth of the PANI film increased. The potential-step growth program involves starting at an initial potential, V_1 for as long as it takes to pass a predetermined amount of coulombs, C_1 . The potential is then stepped ($V_{\text{step}1}$) to the next voltage ($V_2 = V_1 + V_{\text{step}}$) until a predetermined amount of coulombs is passed (C_2). This process is repeated until the voltage max (V_{max}) is reached. This method is referred to as the potential-step PANI process and was carried out on a MACCOR 4000 instrument. Films of 40C were prepared by this method with the potential ramping from +0.750 V to +0.825 V in four steps. Films were discharged to –0.2 V with a 4 mA current in the growth solution (*vide infra*) immediately after deposition to remove sulfate anions from the PANI film.

Aqueous CVs were recorded in pH 1.3 (adjusted with H_2SO_4) solutions (20 ml) vs. Ag/AgCl. Two Pt plates connected in series were used as the counter electrodes and potentials were recorded in the range –0.200 V to +0.800 V vs. Ag/AgCl on PAR 273 or 273A potentiostats. A single compartment electrochemical cell was utilized in this experiment.

2.4. Electrochemical polymerization of PANI on Pt electrodes

Pt electrodes were polished with Alumina 2.0 and cleaned three times with DIW to obtain a clean Pt surface. The Pt electrode was then used for electrodeposition of PANI without further surface modification by immersion in aqueous growth solutions containing 0.45M aniline and 0.1M CSA with the pH (range 1.0–1.6) adjusted with 6 M H_2SO_4 . PANI was electrochemically polymerized by using the constant potential ramp methods in the range +0.750 V to +0.825 V. Films were discharged to –0.2 V with a 4 mA current rate in the growth solution immediately after deposition to remove sulfate anions and to achieve fully reduced PANI films.

2.5. Rinsing and drying procedure

The PANI films were treated with 5% hydrazine at various time under slightly reduced pressure (using a Schlenk line) to facilitate

removal of gaseous reaction products. For example, 20C films were treated with hydrazine for 5 min and 40C films for 10 min. PANi films were dried in a home built infrared oven at 250 °C for 10 min in a capped vial using N₂ as a carrier gas. The dry weights of PANi were averaged over 7 samples (15.3 mg, 15.4 mg, 14.8 mg, 15.1 mg, 14.5 mg, 15.2 mg, and 15.1 mg).

2.6. Scanning electron microscope

An Amray 1820 SEM was used to study the surface morphology of the rinsed and dried PANi films prepared on Al/C and Pt electrodes. In order to enhance the conductivity of the samples during the SEM experiments, all the samples were sputter coated with gold/palladium (20/80) to 31 nm.

2.7. Non-aqueous transfer and testing methods

Rinsed and dried Al/C/PANI or Pt/PANI films were transferred to ACN or ACN/PC (50/50 v/v) solutions containing 0.5 M LiClO₄ under reduced pressure in a capped vial. Non-aqueous CVs were recorded by using PAR 273 or 273A potentiostats in the potential range –0.200 V to +0.800 V with respect to a Ag/AgNO₃ non-aqueous reference electrode.

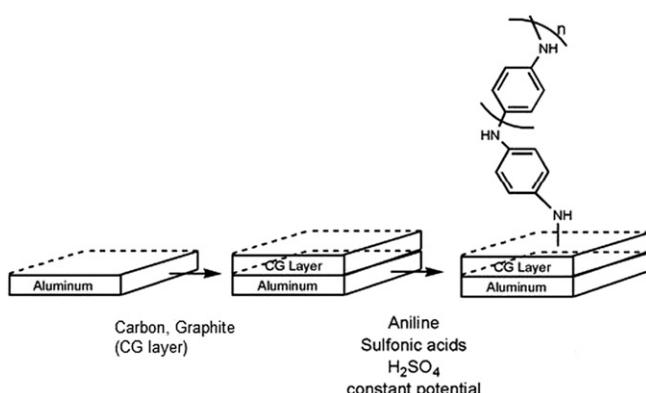
Charge/discharge (CD) capacities of the films were obtained in PC/ACN with a 0.5 M LiClO₄ electrolyte solution using an eight channel MACCOR 4000 series battery tester. A standard two-compartment electrochemical cell, separated with a medium glass frit was used in this study with a fresh Li strip as the counter electrode (in one compartment), and a Ag/AgNO₃ non-aqueous reference electrode.

All the CD tests were carried out in a custom built Terra-universal Glove Box. The charging step was completed with a current rate of 0.5 mA, unless otherwise stated. The end point was determined either by reaching a voltage of +0.810 V, the last half cycle (LHC), or by reaching a predetermined constant miliamphour (mAh) total charge. The discharging step was completed with a current rate of 0.5 mA, unless otherwise stated and the end point voltage of –0.400 V. CD cycles were programmed to run in a loop of a desirable number of cycles, depending on the experimental design.

3. Results and discussion

3.1. Preparation of Al/C electrodes

Scheme 1 summarizes the steps for preparing electrically conductive Al/C/PANI electrodes in acidic aqueous media. Following



Scheme 1. Electrochemical synthesis of Polyaniline on Al/C electrodes.

cleaning of an Al surface, graphite is deposited by rubbing a source of carbon onto the Al surface. PANi is grown directly on this surface in aqueous solutions containing aniline by using electrochemical deposition methods, such as constant current, constant potential, or CV methods. Stable and conductive Al/C/PANI electrodes are produced in aqueous solutions containing aniline, sulfonic acids, and adjusted to low pH with H₂SO₄. Thin strips of Al-1100 or 5052 (1 × 6 cm) were cleaned with acetone and distilled water three times prior to remove surface oil, grease and paint. The cleaned Al surface was then coated with carbon/graphite to completely cover the surface, including the edges. Initially an HB #2 pencil was used to apply the coating on the Al 1100 and 5052 alloy surfaces by gently rubbing the graphite tip against the Al surface in two different directions perpendicular to each other. This action caused an immediate change of the Al surface from a metallic shiny appearance to a gray textured color. The graphite layer applied by this method does not come off when the surface is wiped with a KimWipe, or rinsed with DIW, and/or acetone, suggesting a strong linkage at the Al/C interface.

An alternate method of coating graphite on an Al surface involves using an orbital sander that produces vibration cycles at a rate of about 11,000 per min. A high surface graphite powder (TIMREX, HSAG 300) was used for this coating technique which was carried out for approximately 2 min on each side of an Al electrode sheet. The surface appearance was changed from shiny to a dark gray/black color upon graphite treatment. Al/C electrodes of 1 × 6 cm were cut from the Al/C sheet and the edges were darkened using an HB #2 pencil prior to electrochemical deposition of PANi. The graphite-coated Al surface prepared by this method is also not removed by wiping with a KimWipe or exposing the coated surface to various chemical environments including acetone, ethanol, and DIW.

3.2. Electrochemical deposition of PANi on Al/C electrodes

Electrochemical polymerization of aniline on Al/C electrodes was carried out under various experimental conditions in which the pH, growth potentials, and temperature were modified. The influence of these parameters on the growth rate of PANi is discussed below.

3.2.1. Effect of the growth potential on growth rate

Freshly made Al/C electrodes were used for electrochemical deposition of PANi at 25 °C with the constant potential ramp method and voltage ramping from +0.750 V to +0.825 V vs Ag/AgCl on a MACCOR 4000 series instrument. The growth method was programmed such that a 40C PANi film is produced in 4 steps of 10C each: the process begins with holding the potential at +0.750 V until 10C are reached, then the potential is ramped up to +0.775 V, +0.800 V, and +0.825 V, respectively for subsequent steps. The potential ramp method is efficient in producing large films, up to 40C per 2 cm² sample, by increasing the growth rate (see Fig. 1a). A 40C film can be prepared in about 25 min using this method. In contrast, at a constant potential of +0.788 V (the average potential of the potential ramp method), the growth time is 60% longer (about 40 min) (see Fig. 1b).

3.2.2. Effect of the pH on growth rate

Fig. 2 shows the effect of pH on the growth rate of PANi on Al/C electrodes at 25 °C. The solution pH critically influences the growth of the PANi in aqueous solutions. In electrochemical polymerization of aniline, initiation occurs via formation of a free radical aniline cation by electrooxidation of aniline [26,27]. Formation of free radicals is catalyzed by acidic media and therefore lowering the pH of the growth solution rapidly increases the growth rates (see

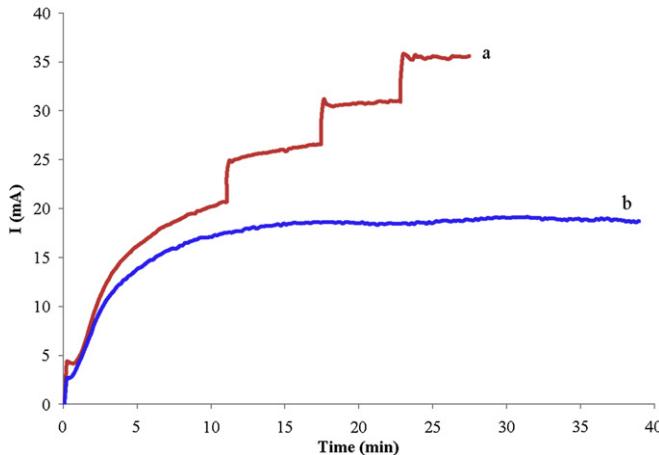


Fig. 1. Growth time to produce 40C films in 0.45 M aniline, 0.1 M CSA at pH 1.3 (adjusted with H_2SO_4) at 25 °C. a. potential-step growth program: $V_{\text{initial}} = +0.750$ V, $C_{1,2,3,4} = 10$ Coulombs, $V_{\text{step}} = +0.025$ V, $V_{\text{final}} = +0.825$ V and b. at a constant potential of +0.788 V.

Fig. 2). However the films produced at pH < 1.0 show poor surface texture upon drying the film. During rapid growth, H_2 may be produced resulting in adsorbed gas trapped inside the film. During the drying process, these bubbles are expelled, which can cause cracking in the film. At pH 1.3, we were able to achieve a relatively rapid growth without destroying the film during the drying process. Therefore we have selected pH 1.3 as the standard pH for our growth solutions.

3.2.3. Effect of the temperature on growth rate

A comparison of growth rates to produce 40C PANi films on Al/C electrodes at different temperatures is shown in Fig. 3. Elevated temperatures result in increasing growth rates in growth solutions of the same composition by increasing the effective current. Although the growth rate is significantly increased at 30 °C, the resulting film shows poor surface texture and delaminates upon drying.

Thus the following parameters were selected for producing PANi films on Al/C electrodes using the potential ramp method: pH = 1.2–1.4 ± 0.1 (adjusted with H_2SO_4) and 25 ± 1 °C. The PANi

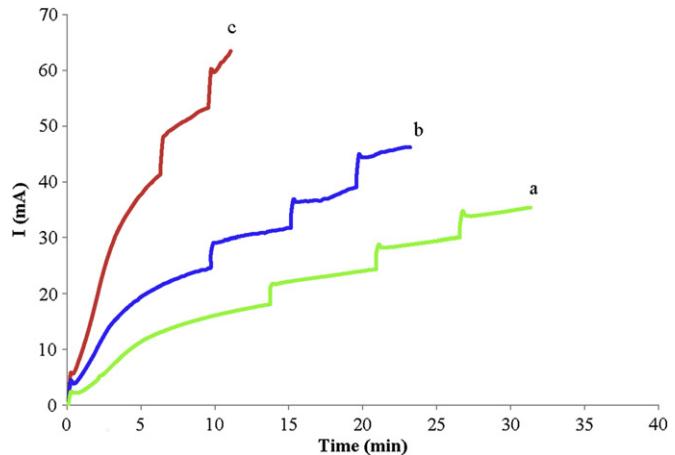


Fig. 3. Growth time to produce 40C films in 0.45 M aniline, 0.1 M CSA at pH 1.3 (adjusted with H_2SO_4) at: a. 19 °C. b. 25 °C and c. 30 °C. Potential-step growth program: $V_{\text{initial}} = +0.750$ V, $C_{1,2,3,4} = 10$ Coulombs, $V_{\text{step}} = +0.025$ V, $V_{\text{final}} = +0.825$ V.

films synthesized on Al/C electrodes by this method show good adhesion to the Al/C electrode surfaces and cannot be completely removed by using 3 M scotch tape [28].

3.3. Comparison of Al/C/PANI and Pt/PANI electrodes

We have also investigated the behavior of Pt electrodes in the electropolymerization of PANi and compared the performance of Pt/PANI electrodes with Al/C/PANI electrodes. In brief, electropolymerization of PANi was carried out in a 0.45 M aniline, 0.1M CSA aqueous solution at pH 1.3 (adjusted with H_2SO_4). A comparison of growth rates of 20C PANi films on Pt and Al/C electrodes at 25 °C is shown in Fig. 4. Both demonstrate adequate growth profiles.

The current response of the electrooxidation of PANi on Al/C electrodes is in the same range as on Pt electrodes. This suggests that the Al/C surface acts in an equivalent manner as a Pt surface for supporting the electropolymerization. However, attempts to prepare PANi films on Al/C electrodes by using growth solutions containing HCl, HClO_4 or HF acids other than H_2SO_4 failed due to rapid oxidation of Al electrode in aqueous media.

The Al/C/PANI and Pt/PANI electrodes also were assessed by using cyclic voltammetry (CV) in aqueous solution at pH 1.3. Cyclic voltammograms of the Al/C/PANI and Pt/PANI are shown in Fig. 5. A

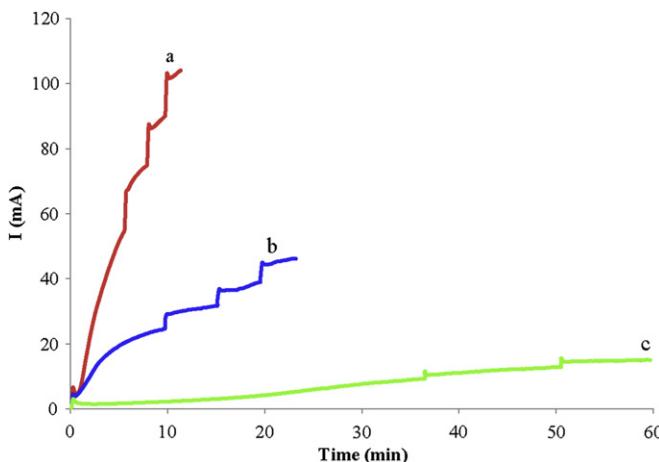


Fig. 2. Growth profiles of 40C PANi films on Al/C electrodes as a function of pH in 0.45 M aniline, 0.1 M CSA; pH adjusted with H_2SO_4 to: a. 0.9 pH, b. 1.3 pH and c. 1.85 pH at 25 °C. Potential-step PANi growth program for films a–c: $V_{\text{initial}} = +0.750$ V, $C_{1,2,3,4} = 10$ Coulombs. $V_{\text{step}} = +0.025$ V, $V_{\text{final}} = +0.825$ V.

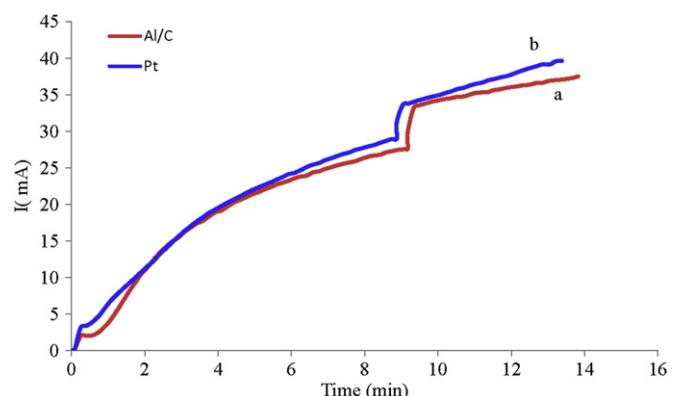


Fig. 4. Growth rates of a. Al/C electrode and b. Pt electrode for 20C PANi films at 25 °C using potentials of +0.750 V and +0.775 V in growth solution containing 0.45 M aniline, 0.1 M CSA and pH 1.3 adjusted with H_2SO_4 .

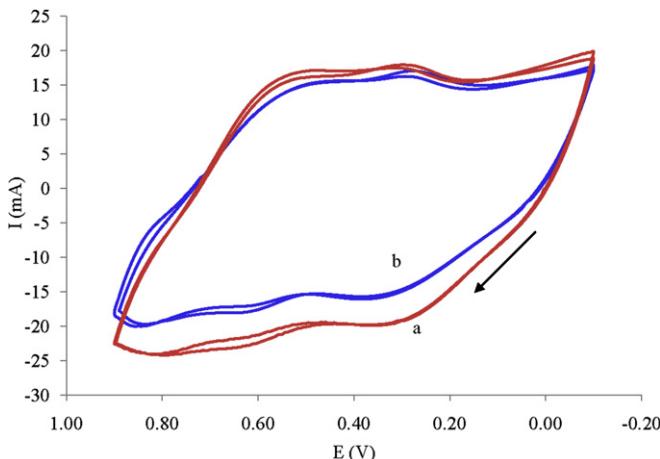


Fig. 5. Aqueous CVs for 20C PANi films at pH 1.3 (adjusted with H_2SO_4) and 4 mV s^{-1} scan rate a. Al/C/PANI (red line) and b. Pt/PANI (blue line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

striking feature of the CVs is that the current response for the Al/C/PANI (red line) is similar to the current response for the Pt/PANI (blue line). The CVs for Al/C/PANI are stable over an extended number of cycles (i.e. 20 cycles) which suggests that the Al/C/PANI electrodes can withstand an acidic environment without showing any degradation.

3.4. Transfer of Al/C/PANI and Pt/PANI electrodes to non-aqueous electrolyte solution

Lithium ion batteries operate in non-aqueous environments with various blends of anhydrous organic solvents such as propylene carbonate (PC), ethylene carbonate, diethyl carbonate, dimethyl carbonate, and acetonitrile (ACN). Therefore it is critically important to transfer PANi films from aqueous solutions to non-aqueous organic solvents prior to the charge/discharge tests. It is equally important to obtain the fully hydrogenated (reduced) form of PANi before the transfer to non-aqueous solution because as previously mentioned by MacDiarmid, it is the only conducting form of PANi in aprotic solvents [29]. As reported by Harada et al., the fully reduced form of PANi can be achieved by treating the film with aqueous hydrazine (a reduced base) [30]. The reduced form of PANi tends to be yellow-green. In our experiments, hydrazine treatments turn the dark PANi films observed at the end of growth at constant potential ($>0.7 \text{ V}$ vs Ag/AgCl) into a light yellow-green film. The amount of time the film is exposed to hydrazine depends on its thickness. We have noticed that prolonged exposure of PANi to 5% hydrazine leads to reduced performance. Therefore the rinsing time was limited to 5 min for 20C PANi films and 10 min for 40C PANi films. The reduced Al/C/PANI or Pt/PANI films were then dried in a homemade infrared oven at 250°C for 10 min under N_2 as a carrier gas. The 40C PANi films prepared according to this method have an average weight of 15 mg.

Following hydrazine treatment and drying, the Al/C/PANI and Pt/PANI electrodes were transferred to an anhydrous blend of PC/ACN (50/50 v/v) with 0.5 M LiClO_4 electrolyte. As shown in Fig. 6, the current response of the CV for Al/C/PANI (red line) is similar to the current response of the CV for Pt/PANI (blue line). On the basis of the experiments discussed thus far, the Al/C/PANI electrodes behave similarly to Pt/PANI electrodes in aqueous and non-aqueous solutions under the conditions described in this paper.

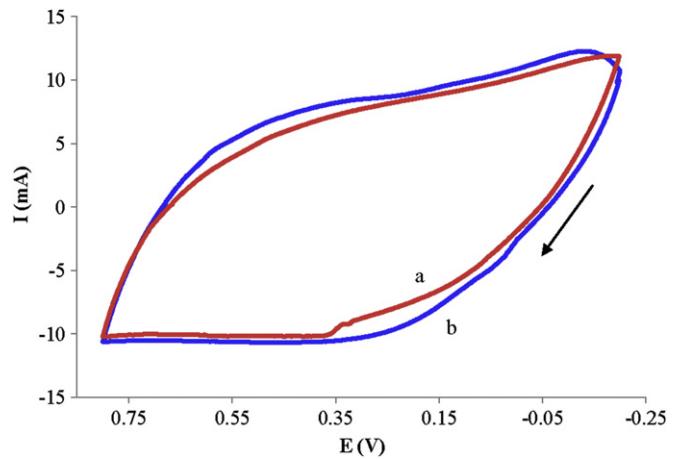


Fig. 6. Non-aqueous CVs for 20C PANi films in PC/ACN (50/50 v/v) with 0.5 M LiClO_4 and 4 mV s^{-1} scan rate a. Al/C/PANI (red line) and b. is Pt/PANI (blue line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.5. Scanning electron microscopy of PANi

SEM images of Al/C/PANI and Pt/PANI electrodes were obtained following hydrazine treatment and drying in an infrared oven for 10 min with N_2 at 250°C . Al/C/PANI images with and without CSA are shown in Fig. 7a and b, respectively. Pt/PANI images with and without CSA are shown in Fig. 7d and e, respectively. The nanofibers of polyaniline appear to form a sponge-like interconnected structure. The morphology of the polyaniline network is identical for Al/C and Pt electrodes with and without CSA. Cross sections of Al/C/PANI and Pt/PANI electrodes reveal that the electrically synthesized PANi is bound to the electrode surfaces (see Fig. 7c and f). Therefore it can be concluded that the PANi grown on Pt electrodes is similar to the PANi grown on Al/C electrodes.

3.6. Comparison of charge/discharge characteristics for Al/C/PANI and Pt/PANI electrodes

Charge/discharge experiments have been conducted with the Al/C/PANI and Pt/PANI electrodes in a PC/ACN solvent mixture containing 0.5M LiClO_4 electrolyte. A MACCOR 4000 series battery tester was used to charge and discharge the polymer films in an Ar-filled glove box at -60°F dew point. Films were charged and discharged at a constant current of 0.5 mA between $+0.8 \text{ V}$ and -0.4 V vs a Ag/AgNO_3 non-aqueous reference electrode and a Li counter electrode. The charge discharge capacities of 30C Al/C/PANI and Pt/PANI electrodes are shown in Fig. 8. These experimental data indicate that the performance of PANi films on Al/C electrodes compares favorably to PANi films on Pt in terms of their ability to store charge in the form of Li ions in anhydrous organic solvents.

Fig. 9 shows the capacity of a 40C Al/C/PANI film in a PC/ACN (50/50 v/v) anhydrous organic solvent mixture over 50 cycles. The performance demonstrates stability. The inset shows the voltage vs total capacity (mAh) when discharged at 0.5 mA constant current between $+0.810 \text{ V}$ and -0.400 V . Theoretically, approximately 2.5×10^{20} electrons are required to make a 40C film. It is reported in the literature that for every 2 electrons passed, the PANi polymer chain increases by one repeat unit [31,32]. Therefore the maximum number of repeat units in the polymer matrix for a 40C film would be 1.25×10^{20} . Based on a monomer unit of $-\text{C}_6\text{H}_4\text{NH}-$ (91.1 amu), the theoretical weight would be $(1.1 \times 10^{20}) \times (91.1 \text{ amu}) \times (1.66 \times 10^{-24} \text{ g amu}^{-1}) = 16.6 \text{ mg}$. This is close to the

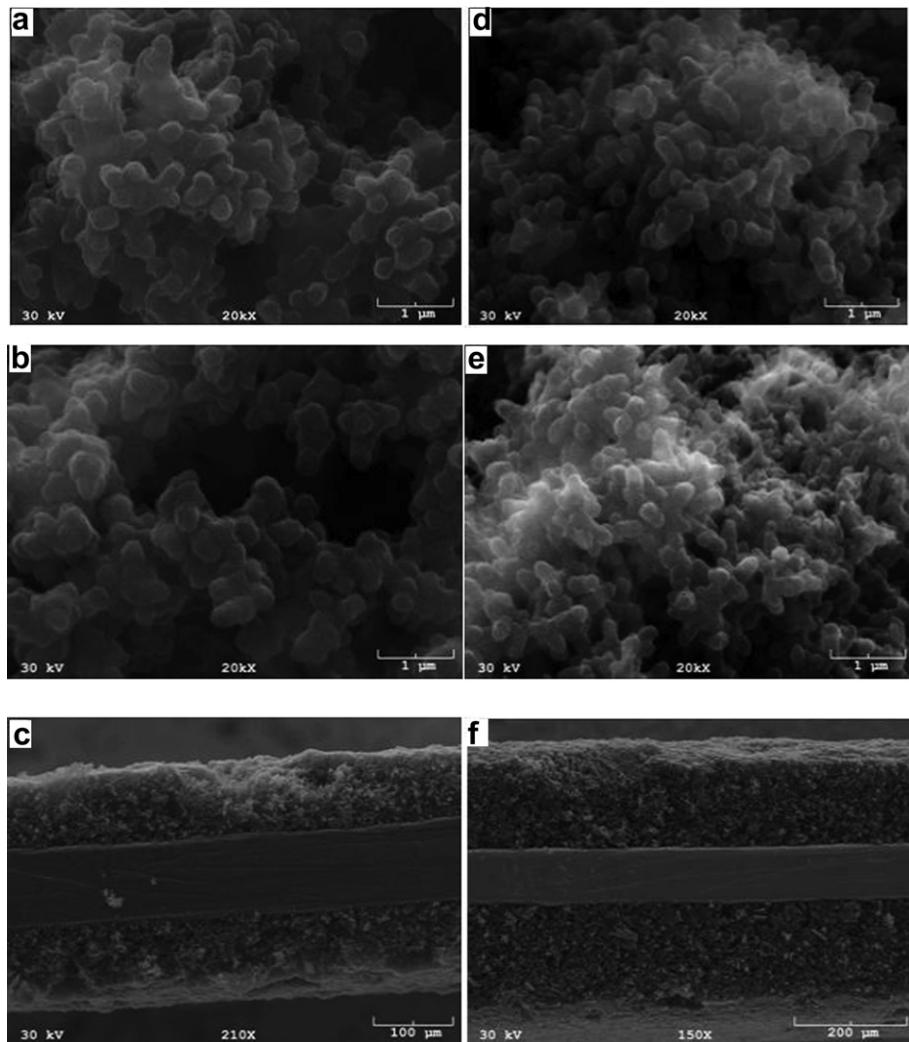


Fig. 7. Scanning electron microscope images of a. Al/C/PANI, b. Al/C/PANI with CSA, c. cross section of Al/C/PANI, d. Pt/PANI, e. Pt/PANI with CSA, and f. cross section of Pt/PANI electrodes.

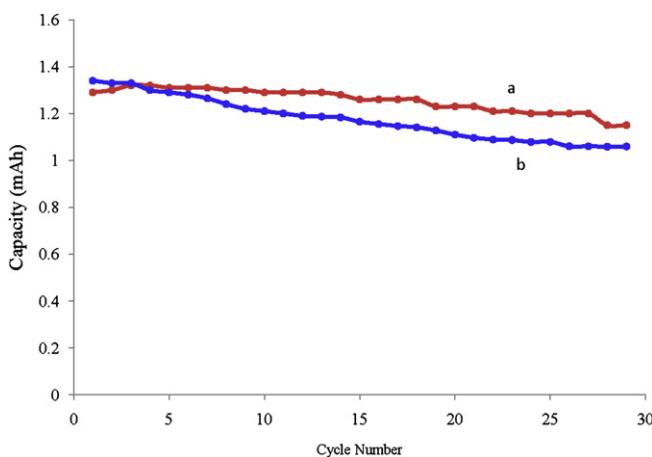


Fig. 8. The discharge capacities of 30C PANI films on a. Al/C and b. Pt electrode. Capacities were obtained in a PC/ACN (50:50) solution containing 0.5 M LiClO₄ with a Li counter electrode. CD current rate is 0.5 mA (C/4) and upper and lower voltage limits are +0.810 V and -0.400 V, respectively.

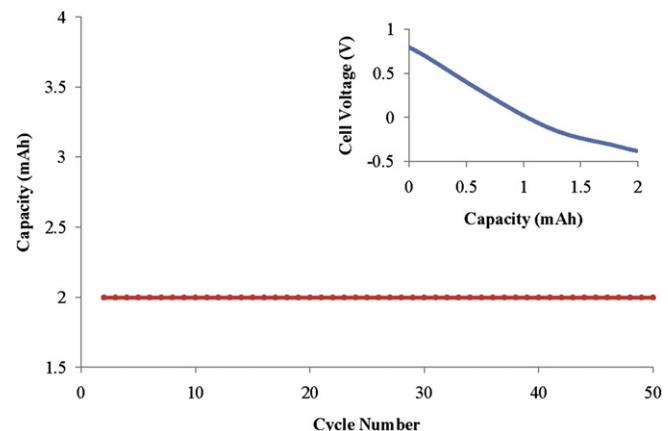


Fig. 9. The discharge capacities for 40C Al/C/PANI film in PC/ACN/0.5M LiClO₄ with a Li counter electrode. CD current rate is 0.5 mA (C/4) and upper and lower voltage limits are +0.810 V and -0.400 V, respectively. Inset: Time based discharge capacity (mAh) with voltage limit of +0.810 V to -0.400 V (vs. Ag/AgNO₃ non-aqueous reference electrode).

average dry weights (15 mg) for the 40C films produced on Al/C/PANI electrodes.

Based on the assumption that one repeat unit can hold one Li^+ ion, the total Li^+ ions that a 40C film can hold would be 1.25×10^{20} . So the theoretical capacity of the 40C film would be 17.4C in non-aqueous electrolyte solutions. Based on the 2.0 mAh discharge (see Fig. 9) the actual capacity of a 40C film in non-aqueous electrolyte solution is 7.2C. This represents an approximate efficiency of 40% of the 40C film in non-aqueous electrolyte solutions. Based on the actual discharge of 2.0 mAh, for a 40C film with a 15 mg dry weight, the specific capacity of the film is 133 mAh g⁻¹, which is in the range of reported values in the literature [5,33–35].

4. Conclusion

We report a simple and reliable method to electrochemically synthesize PANi on aluminum carbon (Al/C) surfaces in acidic aqueous solutions. The fabrication of conductive PANi polymers is carried out electrochemically on Al/C electrodes, which are prepared by applying a layer of graphite on a clean Al alloy surface (1100 and 5052 series). The resulting PANi films are stable upon transfer to non-aqueous solvents. Charge/discharge performance studies and SEM images demonstrate similar results for Pt/PANI and Al/C/PANI electrodes suggesting that Al/C/PANI composite electrodes behave in a similar fashion to Pt/PANI composite electrodes under the conditions described in this paper. The composite Al/C/PANI electrodes were evaluated by conducting charge-discharge experiments on a MACCOR multi channel instrument: the 40C PANi films on Al/C electrodes operate at about 40% efficiency and have a specific capacity of *ca.* 133 mAh g⁻¹. This is in good agreement with reported data for other PANi-based electrodes. The results suggest that a new generation of energy storage devices may be developed based on PANi films built on carbon–aluminum electrodes.

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